# Influence of Trehalose, Glucose, Fructose, and Sucrose on Gelatinisation and Retrogradation of Corn and Tapioca Starches

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### Abstract

BABIĆ J., ŠUBARIĆ D., MILIČEVIĆ B., AČKAR D., KOPJAR M., NEDIC TIBAN N. (2009): **Influence of trehalo**se, glucose, fructose, and sucrose on gelatinisation and retrogradation of corn and tapioca starches. Czech J. Food Sci., **27:** 151–157.

The effects of trehalose, glucose, fructose, and sucrose on the gelatinisation and retrogradation properties of corn (CS) and tapioca (TS) starches were studied with differential scanning calorimetry (DSC). The results showed that the sugars affect gelatinisation and retrogradation of both starches, with the effect varying significantly between sugars. The addition of trehalose, glucose, fructose, and sucrose increased the gelatinisation temperatures and enthalpy of gelatinisation of corn and tapioca starches. The extent of increase followed the order: fructose < glucose < tre-halose < sucrose with CS, and fructose < trehalose < sucrose < glucose with TS. The retrogradation studies showed that sugars of lower molecular weights (glucose and fructose) were less effective in the reduction of retrogradation than those of higher molecular weights (sucrose and trehalose). Trehalose retarded retrogradation of both corn and tapioca starches under all conditions investigated. Sucrose had the same effect on the corn starch retrogradation. The effects of other sugars depended on the type of starch, storage period, and storage temperature.

Keywords: corn starch; tapioca starch; sugars; gelatinisation; retrogradation

Starch is widely used in food industry as a thickening agent or stabiliser, to provide control of moisture and water mobility, improve the overall product quality, reduce cost, and/or facilitate the processing (SHI & BEMILLER 2002; FUNAMI *et al.* 2005). Its functionality depends on the molecular structure of the amylose and amylopectin components and their interactions with the environ-

ment during two main processes, gelatinisation and retrogradation (LEWEN *et al.* 2003). Sugars are important ingredients in many food products which contain starch, affecting properties such as gelatinisation, retrogradation, and staling. Thus, it is important to understand the interactions between sugars and starch to achieve the desired properties and stability of products.

Supported by the Ministry of Science, Education, and Sports of the Republic of Croatia, Project "Development of new modified starches and their application in food industry".

Gelatinisation of starch is phase transition of starch granules from an ordered to a disordered state during heating with excess water. It induces a number of changes in starch granules, such as swelling, exudation of amylose and amylopectin, granule disruption, loss of birefringence, and increased viscosity (ALAVI 2003; LI et al. 2004). The texture and acceptability of starch-containing foods correlates with retrogradation of starch which has been mainly described as the recrystallisation process of the gelatinised starch. The retrogradation rate is affected by the ratio of amylose and amylopectin, molecular size, temperature, pH, lipids, hydrocolloids, sugars and botanical sources (AEE et al. 1998). Gelatinisation and retrogradation of starch have been intensively investigated with differential scanning calorimetry (DSC) (SOPADE et al. 2004; Koo et al. 2005; Zhong & Sun 2005; Вавіс *et al.* 2006а).

The results of several studies agree that sugars increase the gelatinisation temperature of starch (JOHNSON *et al.* 1990; HOOVER & SENANAYAKE 1996; PERRY & DONALD 2002; BABIC *et al.* 2006b). Many mechanisms have been proposed to explain this phenomenon: starch-sugar interaction (HAN-SEN *et al.* 1989; LIM *et al.* 1992), the formation of starch-sugar inclusion complexes (TOMASIK *et al.* 1995), the increase in the free volume resulting in a lesser plasticising effect of the starch-sugar solvent (LEVINE & SLADE 1989), and the ability of sugar to compete for water with starch and reduce the water activity (DERBY *et al.* 1975).

Early studies showed that sugars influence the starch retrogradation. However, the literature is replete with conflict information about the influence of individual sugars on retrogradation. Конуама and NISHINARI (1991) reported that sugars prevented the retrogradation of sweet potato starch paste and they proposed that sugar molecules interact with the starch molecular chain to stabilise the starch matrix, thus inhibiting retrogradation. L'ANSON *et al.* (1990) showed by means of X-ray diffraction and rheological studies that the crystallinity development in wheat starch gels was reduced in the presence of sugars. The effectiveness of the sugars examined followed the order: ribose < sucrose < glucose (starch:sugar:water 1:1:1). MAX-WELL and ZOBEL (1978), CHANG and LIU (1991), WARD et al. (1994), however, reported that sugar enhanced the starch gel retrogradation.

It is obvious from various studies that sugars significantly influence the thermal properties of starch, the effect depending on the type of sugar, nature of the starch, and storage conditions. The aim of this research was to investigate the effects of trehalose, glucose, fructose, and sucrose on the gelatinisation and retrogradation of corn and tapioca starches at different storage temperatures. In this study, differential scanning calorimetry (DSC) was used to characterise the modifications in the starch gelatinisation and retrogradation caused by the addition of sugars.

## MATERIAL AND METHODS

Corn starch (moisture content 8.61%) was obtained from Agrana, Austria. Tapioca starch (moisture content 13.6%) was obtained from International Starch Trading, Aarhus, Denmark. Glucose, fructose, and sucrose were products of Fluka, Switzerland. Trehalose was obtained from Sigma-Aldrich Chemie, Germany.

The gelatinisation and retrogradation properties were analysed using differential scanning calorimeter DSC 822<sup>e</sup> (Mettler Toledo) equipped with STAR<sup>e</sup> software. An empty pan was used as a reference. Corn or tapioca starch was weighed into the standard aluminium pan (40 µl). Distilled water or an appropriate sugar solution of glucose, fructose, sucrose, or trehalose was added to the starch to give 4:6 starch:water ratio with sugars being 20% g/g dry starch. Pans were sealed and equilibrated for 24 h at the room temperature before the heat treatment in the DSC. The starch slurry was gelatinised in the DSC using a heat rate of 10°C/min from 25°C to 95°C. After the heat treatment, the samples were cooled to 25°C and removed from DSC. The starch gels were aged at 4°C and 25°C and monitored for retrogradation after 7 and 14 days. The retrogradation experiments were conducted at a heating rate of 10°C/min from 25°C to 95°C. The changes in enthalpy ( $\Delta H$  in J/g of dry starch), onset temperature (T<sub>o</sub>), peak temperature  $(T_p)$ , and conclusion temperature  $(T_c)$  for gelatinisation and retrogradation were obtained from the exotherm DSC curves. The experiments were run in triplicates.

**Statistical analyses.** The experimental data were analysed by the analysis of variance (ANOVA) and Fisher's least significant difference (LSD) with significance defined at P < 0.05. All statistical analyses were carried out using the software program STATISTICA 7 (StatSoft, Inc., USA).

### **RESULTS AND DISCUSSION**

Table 1 shows the onset temperature, peak temperature, conclusion temperature, and enthalpy of gelatinisation for corn and tapioca starch suspensions with and without added trehalose, glucose, fructose, and sucrose. The gelatinisation temperatures  $(T_o, T_p, and T_c)$  shifted to higher values and  $\Delta H_{gel}$  increased with the addition of sugars (20% g/g) (except CS with sucrose).

The gelatinisation temperatures of CS and TS were 2°C to 4°C higher in the sugars solutions. The extent of increase followed the order: fructose < glucose < trehalose < sucrose for CS, and fructose < trehalose < sucrose < glucose for TS. CS with the addition of sucrose appeared to have the highest values of  $\rm T_{o}, \rm T_{p},$  and  $\rm T_{c}$  (67.9, 73.8, and 81.6°C), respectively, and the lowest heat of gelatinisation (9.42 J/g) among all CS samples, while TS with the added glucose had the highest values of the gelatinisation temperatures (68.2, 73.5, and 87.9°C) and  $\Delta H_{gel}$  (15.88 J/g). Fructose had the lowest effect on the gelatinisation temperatures increase with both CS and TS. These results are in agreement with those reported in the literature (AEE et al. 1998; BABIC et al. 2006a, b), and some of the mechanisms proposed for such an effect have been mentioned above.

It has been reported that retrogradation consists of two separable processes (MILES *et al.* 1985). The

first stage is governed by the gelation of amylose solubilised during gelatinisation, and the second stage is induced by the recrystallisation of amylopectin within the gelatinised granules. The enthalpy of recrystallised starch melting is lower than that of gelatinisation, in agreement with the fact that the melting of recrystallised starch during storage is always easier than the melting of native starch granules (DURAN *et al.* 2001).

The results obtained for the retrogradation parameters of corn and tapioca starches with and without added trehalose, glucose, fructose, and sucrose are shown in Tables 2 and 3. The retrogradation ratio increased with time and at a lower temperature.

In Table 2 are shown the retrogradation characteristics of 40% corn starch gels, with and without added sugars, after 7 and 14 days at 25°C. Sucrose and trehalose additions caused a decrease, while those of glucose and fructose caused an increase of retrogradation of CS gels at 25°C, with the effect following the order: sucrose < trehalose < no addition < glucose < fructose. Retrogradation enthalpies varied from 3.06-4.17 J/g (control sample, 3.54 J/g) for the storage period of 7 days, and from 4.40-5.57 J/g (control sample 5.34 J/g) for the storage period of 14 days.

During storage at 4°C of the CS samples with and without the addition of sugars, only fructose slightly increased  $\Delta H_{ret}$  of CS gels after 14 days of

Table 1. Differential scanning calorimetry of gelatinisation properties of corn and tapioca starch suspensions (40%) with and without added trehalose, glucose, fructose, and sucrose (20% g/g)

Sample	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	$\Delta H_{gel} (J/g)$
CS	$64.7^{a} \pm 0.02$	$70.3^{a} \pm 0.06$	$77.5^{a} \pm 0.05$	$9.68^{\rm b} \pm 0.03$
CS + trehalose	$67.6^{d} \pm 0.14$	$73.5^{d} \pm 0.18$	$81.4^{d}\pm0.18$	$11.07^{\rm d} \pm 0.07$
CS + glucose	$67.2^{\circ} \pm 0.11$	$72.9^{\circ} \pm 0.12$	$80.5^{\circ} \pm 0.14$	$11.14^{\rm d}\pm0.08$
CS + fructose	$66.7^{b} \pm 0.06$	$72.3^{b} \pm 0.01$	$79.8^{b}\pm0.08$	$10.72^{\circ} \pm 0.04$
CS + sucrose	$67.9^{\rm e} \pm 0.15$	$73.8^{\rm e} \pm 0.19$	$81.6^{\rm d}\pm0.18$	$9.42^{a} \pm 0.03$
TS	$64.8^{a} \pm 0.07$	$69.9^{a} \pm 0.12$	$84.6^{a} \pm 0.07$	$14.31^{a} \pm 0.09$
TS + trehalose	$68.0^d \pm 0.02$	$72.9^{\rm b} \pm 0.03$	$86.5^{b} \pm 0.09$	$14.36^{ab} \pm 0.1$
TS + glucose	$68.2^{d}\pm0.12$	$73.5^{\circ} \pm 0.08$	$87.9^{\circ} \pm 0.11$	$15.88^{d} \pm 0.07$
TS + fructose	$67.4^{c} \pm 0.14$	$72.6^{b} \pm 0.11$	$86.6^{\rm b}\pm0.18$	$14.65^{\rm b} \pm 0.04$
TS + sucrose	$65.6^{b} \pm 0.17$	$73.7^{\rm c} \pm 0.16$	$87.5^{c} \pm 0.06$	$15.49^{\circ} \pm 0.11$

CS – corn starch; TS – tapioca starch; T<sub>o</sub> – onset temperature; T<sub>p</sub> – peak temperature; T<sub>c</sub> – conclusion temperature;  $\Delta H_{gel}$  – gelatinisation enthalpy; the values are means ± SD of triplicates; values in the same column with different superscripts (a–e) are significantly different (P < 0.05)

Sample	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	$\Delta H_{ret} (J/g)$				
Storage at 4°C								
CS	$41.7^{a} \pm 0.03$	$52.1^{a} \pm 0.08$	$63.4^{a} \pm 0.15$	$5.64^{d} \pm 0.01$				
CS + trehalose	$42.0^{b} \pm 0.03$	$53.1^{b} \pm 0.08$	$65.1^{\mathrm{b}} \pm 0.02$	$5.45^{c} \pm 0.02$				
CS + glucose	$41.9^{b} \pm 0.19$	$53.1^{b} \pm 0.02$	$65.0^{\rm b}\pm0.11$	$5.42^{c} \pm 0.02$				
CS + fructose	$43.2^{c} \pm 0.13$	$53.5^{c} \pm 0.15$	$65.9^{\circ} \pm 0.19$	$5.33^b\pm0.05$				
CS + sucrose	$41.6^{a} \pm 0.15$	$52.3^{a} \pm 0.05$	$65.6^{\rm c} \pm 0.10$	$4.66^{a} \pm 0.03$				
CS	$41.4^{a} \pm 0.09$	$51.8^{a} \pm 0.11$	$64.0^{a} \pm 0.12$	$6.17^{b} \pm 0.06$				
CS + trehalose	$42.1^b\pm0.02$	$53.2^{\rm c} \pm 0.26$	$65.1^{\mathrm{b}} \pm 0.02$	$6.15^b\pm0.20$				
CS + glucose	$41.9^{\rm b}\pm0.24$	$53.2^{\circ} \pm 0.08$	$65.1^{b} \pm 0.21$	$6.06^{\rm b}\pm0.12$				
CS + fructose	$43.1^{\circ} \pm 0.09$	$53.8^{d} \pm 0.01$	$66.0^{c} \pm 0.12$	$6.69^{\circ} \pm 0.08$				
CS + sucrose	$41.8^{b}\pm0.16$	$52.9^{\rm b} \pm 0.14$	$65.4^{\mathrm{b}} \pm 0.19$	$5.76^{a} \pm 0.04$				
Storage at 25°C								
CS	$52.2^{a} \pm 0.11$	$61.3^{a} \pm 0.08$	$69.9^{a} \pm 0.21$	$3.54^{\circ} \pm 0.07$				
CS + trehalose	$53.1^{\circ} \pm 0.19$	$62.3^{\circ} \pm 0.04$	$70.7^{\mathrm{b}} \pm 0.21$	$3.26^{b}\pm0.04$				
CS + glucose	$52.5^{b} \pm 0.11$	$61.9^{\rm b} \pm 0.18$	$71.5^{c} \pm 0.07$	$4.05^{d} \pm 0.01$				
CS + fructose	$52.7^{\mathrm{b}} \pm 0.12$	$62.4^{c} \pm 0.11$	$72.1^{d} \pm 0.15$	$4.17^{\rm e} \pm 0.03$				
CS + sucrose	$53.2^{\circ} \pm 0.04$	$61.9^{\rm b} \pm 0.04$	$70.9^{\rm b} \pm 0.13$	$3.06^{a} \pm 0.07$				
CS	$51.9^{a} \pm 0.07$	$61.6^{a} \pm 0.07$	$70.6^{a} \pm 0.09$	$5.34^{\rm c} \pm 0.03$				
CS + trehalose	$52.8^{b} \pm 0.16$	$62.6^{b} \pm 0.18$	$71.1^{b} \pm 0.25$	$4.92^{\mathrm{b}}\pm0.07$				
CS + glucose	$52.9^{b} \pm 0.15$	$62.7^{\rm b} \pm 0.17$	$71.6^{\circ} \pm 0.05$	$5.47^{cd} \pm 0.04$				
CS + fructose	$53.3^{c} \pm 0.10$	$63.2^{\circ} \pm 0.08$	$72.4^{d} \pm 0.09$	$5.57^{d} \pm 0.08$				
CS + sucrose	$53.3^{\circ} \pm 0.10$	$62.6^{\rm b} \pm 0.17$	$71.3^{bc}\pm0.19$	$4.40^{a} \pm 0.01$				
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Table 2. Retrogradation characteristics of 40% corn starch gels with and without added trehalose, glucose, fructose, and sucrose after 7 days and 14 days of storage at 4°C and 25°C

CS – corn starch;  $T_o$  – onset temperature;  $T_p$  – peak temperature;  $T_c$  – conclusion temperature;  $\Delta H_{ret}$  – retrogradation enthalpy; the values are means ± SD of triplicates; values in the same column with different superscripts (a–e) are significantly different (P < 0.05)

storage (for 0.52 J/g). The retrogradation enthalpy values of the CS samples stored at 4°C follows the order: sucrose < fructose < glucose < trehalose < no addition after 7 days; sucrose < glucose < trehalose < no addition < fructose after 14 days (Table 2).

Table 3 shows the retrogradation characteristics of 40% tapioca gels, with and without added sugars after 7 days and 14 days at 25°C. All added sugars caused a decrease of TS gels retrogradation after 7 days of storage, while only trehalose decreased retrogradation after 14 days of storage at 25°C. The retrogradation enthalpy values of the TS samples stored at 25°C followed the order: trehalose < glucose < fructose < sucrose < no addition after 7 days; trehalose < no addition < sucrose < fructose < glucose after 14 days. Retrogradation enthalpies varied from 3.76–5.27 J/g (control sample, 5.27 J/g) for the storage period of 7 days, and from 5.06 to 6.48 J/g (control sample 5.80 J/g) for the storage period of 14 days.

At the storage temperature of 4°C after 7 days and 14 days of storage of the TS samples, only sucrose slightly increased retrogradation of TS gels (for 0.35 J/g). The retrogradation enthalpy values of the TS samples with and without the addition of sugars stored at 4°C follows the order: fructose < trehalose < glucose < no addition < sucrose after

	Sample	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	$\Delta Hr_{ret} (J/g)$
Stora	ge at 4°C				
After 7 days	TS	$49.8^{a}\pm0.12$	$59.9^{a} \pm 0.21$	$70.7^{a} \pm 0.13$	$5.27^{c} \pm 0.08$
	TS + trehalose	$52.1^{d} \pm 0.19$	$62.4^{e} \pm 0.29$	$72.0^{\rm b} \pm 0.18$	$3.76^{a} \pm 0.19$
	TS + glucose	$51.1^{c} \pm 0.08$	$60.8^{b} \pm 0.17$	$72.3^{bc} \pm 0.14$	$4.60^{\rm b}\pm0.12$
	TS + fructose	$51.7^{c} \pm 0.18$	$61.9^{d} \pm 0.08$	$72.4^{c} \pm 0.07$	$4.64^{\rm b}\pm0.12$
	TS + sucrose	$50.7^b\pm0.04$	$61.5^{\circ} \pm 0.19$	$72.6^{\circ} \pm 0.09$	$4.82^{b}\pm0.08$
After 14 days	TS	$52.4^{bc} \pm 0.17$	$62.3^{a} \pm 0.16$	$71.3^{a} \pm 0.13$	$5.80^{\rm b} \pm 0.11$
	TS + trehalose	$53.7^{d} \pm 0.15$	$63.2^{d} \pm 0.21$	$72.5^{\rm b} \pm 0.12$	$5.06^{a} \pm 0.07$
	TS + glucose	$52.1^{ab} \pm 0.08$	$62.9^{cd} \pm 0.09$	$72.6^{\rm b} \pm 0.08$	$6.48^{\circ} \pm 0.06$
	TS + fructose	$51.8^{a} \pm 0.12$	$62.6^{bc} \pm 0.05$	$73.0^{\circ} \pm 0.05$	$6.43^{c} \pm 0.07$
	TS + sucrose	$52.5^{c} \pm 0.09$	$62.7^{c} \pm 0.12$	$72.5^{\rm b} \pm 0.11$	$5.81^{b} \pm 0.12$
Stora	ge at 25°C				
After 7 days	TS	$39.9^{a} \pm 0.14$	$53.7^{bc}\pm0.04$	$64.1^{a} \pm 0.11$	$5.99^{\rm b} \pm 0.09$
	TS + trehalose	$42.0^{a} \pm 0.03$	$53.1^{a} \pm 0.08$	$65.1^{b} \pm 0.23$	$5.45^{a} \pm 0.02$
	TS + glucose	$42.3^{a} \pm 0.18$	$53.8^{\circ} \pm 0.06$	$67.0^{\rm e} \pm 0.15$	$5.83^{b} \pm 0.11$
	TS + fructose	$42.9^{b} \pm 0.25$	$53.4^{ab} \pm 0.27$	$65.9^{\circ} \pm 0.03$	$5.27^{a} \pm 0.10$
	TS + sucrose	$42.1^{a} \pm 0.21$	$53.5^{bc} \pm 0.20$	$66.5^{d} \pm 0.06$	$6.34^{\rm c} \pm 0.08$
	TS	$39.9^{a} \pm 0.07$	$50.9^{a} \pm 0.13$	$64.6^{a} \pm 0.12$	$7.47^{\rm b} \pm 0.11$
After 14 days	TS + trehalose	$41.3^{\circ} \pm 0.07$	$52.8^{d} \pm 0.21$	$65.8^{\rm b} \pm 0.04$	$7.19^{\rm b} \pm 0.08$
	TS + glucose	$40.1^{a} \pm 0.14$	$51.9^{\rm b} \pm 0.08$	$66.6^{\circ} \pm 0.09$	$7.44^{\rm b}\pm0.08$
	TS + fructose	$40.9^{\rm b}\pm0.18$	$52.3^{\circ} \pm 0.02$	$66.1^{b} \pm 0.17$	$6.71^{a} \pm 0.03$
	TS + sucrose	$41.9^{\rm d} \pm 0.21$	$52.8^{d} \pm 0.21$	$66.9^{\circ} \pm 0.08$	$7.34^{\rm b}\pm0.04$

Table 3. Retrogradation characteristics of 40% tapioca starch gels with and without added trehalose, glucose, fructose, and sucrose after 7days and 14 days of storage at 4°C and 25°C

TS – tapioca starch;  $T_o$  – onset temperature;  $T_p$  – peak temperature;  $T_c$  – conclusion temperature;  $\Delta H_{ret}$  – retrogradation enthalpy; the values are means ± SD of triplicates; values in the same column with different superscripts (a–e) are significantly different (P < 0.05)

7 days; fructose < trehalose < sucrose < glucose < no addition after 14 days (Table 3).

Sugars do affect the melting temperature of the retrograded starch and the extent to which retrogradation occurs (HOOVER 1995). In this work, sugars caused a slight increase in the melting temperatures  $(1-2^{\circ}C)$  of recrystallised CS and TS after 7 days and 14 days at 4°C and 25°C. After storage at the lower temperature, the differences in the peak melting temperatures were higher and ranged between 51.8–53.8°C for CS, and 50.9–53.8°C for TS (Tables 2 and 3).

Our results show that trehalose retarded the retrogradation of both corn and tapioca starch under all conditions investigated. Sucrose had the same effect on the corn starch retrogradation. The effects of other sugars depended on the type of starch, storage period, and storage temperature. CHANG and LIU (1991) reported that sucrose promoted the retrogradation of rice starch, and SLADE and LEVINE (1987) showed that fructose promoted the retrogradation of wheat starch. Other researches (KOHYAMA & NISHINARI 1991; BELLO-PEREZ & OARADEZ-LOPEZ 1995) showed by means of DSC measurements that sucrose and glucose inhibit the retrogradation of wheat, amaranth, waxy corn, and sweet potato starches. This also suggests that the increase or decrease in retrogradation in the presence of sugars is influenced by the starch source. Out of the sugars investigated, glucose and fructose were more effective in promoting retrogradation than sucrose or trehalose, since the interaction with the branched amylopectin chains is more difficult with larger sucrose or trehalose molecules.

## CONCLUSIONS

The gelatinisation temperatures shifted to higher values and the enthalpy of gelatinisation increased with the addition of trehalose, glucose, fructose, and sucrose. The extent of increase followed the order: fructose < glucose < trehalose < sucrose for CS, and fructose < trehalose < sucrose < glucose for TS.

Sugars of lower molecular weights (glucose and fructose) were less effective in the reduction of retrogradation than those of higher molecular weights (sucrose or trehalose). Trehalose retarded the retrogradation of both corn and tapioca starch under all conditions investigated. Sucrose had same effect on corn starch retrogradation. The effects of other sugars depended on the type of starch, storage period, and storage temperature.

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Received for publication February 12, 2009 Accepted after corrections June 24, 2009

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